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## Thermodynamics of Adduct-Formation of *Bis*(3-trifluoroacetyl-*d*-camphorato)copper (II) with Pyridines

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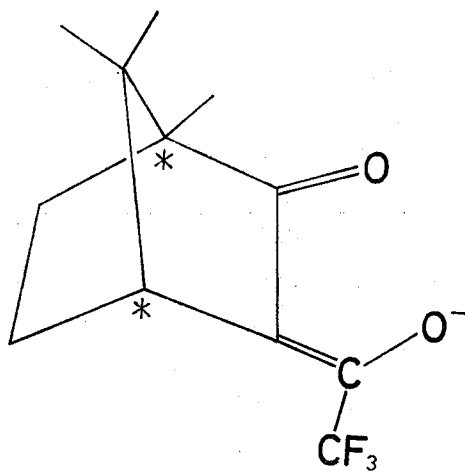
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Thermodynamic data was obtained for the reaction in benzene solution of *bis*(3-trifluoroacetyl-*d*-camphorato)copper (II) with pyridines. The enthalpy change of the adduct formation with pyridine is  $-6.8$  Kcal/mol which is similar to that of  $\text{Cu}(\text{tfa})_2$ . The enthalpy changes of the adduct formation with  $\beta$ - and  $\gamma$ -picolines are unusually large. The  $\Delta H$  value of  $\alpha$ -picoline is  $-8.3$  Kcal/mol.

Some metal complexes of  $\beta$ -diketones react further with heterocyclic bases, amines, and phosphate esters.<sup>1~4)</sup> Recently, the thermodynamics of adduct formation has been studied in comparatively few systems.<sup>5~11)</sup> The stability of 1:1- and 1:2-adducts is sensitively affected by the introduction of substituted groups into  $\beta$ -diketones. We reported about the adduct formation of *bis*(3-trifluoroacetyl-*d*-camphorato)copper(II),  $\text{Cu}(\text{facam})_2$ , possessing the rigid and bulky  $\beta$ -diketone.<sup>12)</sup> This time we have investigated the thermodynamic property of the adduct formation of  $\text{Cu}(\text{facam})_2$  with the pyridines and will report the results in this paper.

### EXPERIMENTAL

**Materials.** All the pyridines were stocked in the addition of potassium hydroxide and distilled prior to use. Reagent grade benzene was used as solvent.



facam

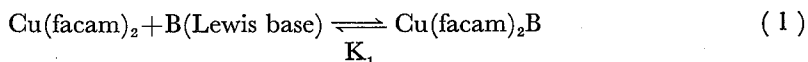
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**3-Trifluoroacetyl-*d*-camphor, (Hfacam).** 3-Trifluoroacetyl-*d*-camphor was prepared using a procedure similar to that for the synthesis of sterically hindered  $\beta$ -diketones.<sup>13)</sup> Ethyl trifluoroacetate (50 g) and 35 g of sodium hydride dispersed in mineral oil (50% hydride by weight) were added to 460ml of dimethoxyethane. The mixture was stirred sufficiently and brought to the reflux temperature. *d*-Camphor (60.8 g) in 50ml of dimethoxyethane was added from a dropping funnel over a 2-hr period. Gas evolution ceased about 20 min after addition was completed. Concentrated hydrochloric acid (85ml) was added as rapidly as possible to the cooled mixture. Before addition was complete, the suspension became clear and a fine white precipitate formed. The mixture was then cooled and poured into 920ml of water. Pentane (230ml) was added and the organic layer was separated, washed with five 230ml portions of water and then dried over sodium sulfate anhydride all day long. After the solvent was removed by distillation, the residue was distilled. Hfacam was collected at 57°C (1.5 mmHg).

**Bis(3-trifluoroacetyl-*d*-camphorato)copper(II), Cu(II)(facam)<sub>2</sub>.** The complex was prepared by adding an ethanol solution of the ligand to an aqueous solution of copper acetate at 60°C. After cooling, the green crystals which precipitated were filtered off. This product was recrystallized from benzene and then sublimed three times in vacuo at 160°C. Found: C, 51.54; H, 5.14; F, 20.37%. Calcd for C<sub>24</sub>H<sub>28</sub>O<sub>4</sub>F<sub>6</sub>Cu: C, 51.66; H, 5.06; F, 20.43%.

**Apparatus.** Optical absorption measurements were made with Hitachi 323 automatic recording spectrophotometer equipped with a thermostated cell holder which was held at the required temperature by water from the cooling device. The temperature of the solutions was maintained constant within  $\pm 0.1^\circ$ .

**Calculation of formation constants.** The reactions of Lewis bases with Cu(facam)<sub>2</sub> are of the type given below.



The formation constant of the reactions was defined according to:

$$K_1 = \frac{[\text{Cu(facam)}_2\text{B}]}{(C_A - [\text{Cu(facam)}_2\text{B}])(C_B - [\text{Cu(facam)}_2\text{B}])} \quad (2)$$

where  $C_A$  and  $C_B$  are the initial concentrations of Cu(facam)<sub>2</sub> and B, respectively and [Cu(facam)<sub>2</sub>B], the concentration of Cu(facam)<sub>2</sub>B. The absorbance of the system at a chosen wavelength where the Lewis bases exhibit no absorption is

$$A = \epsilon_1(C_A - [\text{Cu(facam)}_2\text{B}]) + \epsilon_2[\text{Cu(facam)}_2\text{B}] \quad (3)$$

where  $\epsilon_1$  and  $\epsilon_2$  are the extinction coefficients of Cu(facam)<sub>2</sub> and Cu(facam)<sub>2</sub>B, respectively. Equations (2) and (3) give Eq. (4):

$$\frac{C_A C_B}{A - A_0} = \left[ C_A + C_B - \frac{A - A_0}{\epsilon_2 - \epsilon_1} \right] \frac{1}{\epsilon_2 - \epsilon_1} + \frac{1}{(\epsilon_2 - \epsilon_1) K_1} \quad (4)$$

where  $A$  and  $A_0$  are the absorbances at a chosen wavelength in the presence and absence of  $B$ .  $K_1$  and  $\epsilon_2$  cannot be evaluated at the same time according to Eq. (4). When  $[\text{Cu}(\text{facam})_2B]$  is far smaller than  $C_A$  and  $C_B$ , Eq. (4) is transformed into Eq. (5):

$$\frac{C_A}{A-A_0} = \left( C_A + \frac{1}{K_1} \right) \frac{1}{(\epsilon_2 - \epsilon_1)C_B} - \frac{1}{\epsilon_2 - \epsilon_1} \quad (5)$$

and  $K_1$  and  $\epsilon_2$  are obtained from the plots of  $C_A/(A-A_0)$  vs.  $1/C_B$  at various concentrations of  $B$ .

### RESULTS AND DISCUSSION

The spectral change of  $\text{Cu}(\text{facam})_2$  in benzene caused by the addition of  $\beta$ -picoline at  $15^\circ\text{C}$  is shown in Fig. 1. When the concentration ratio of  $\beta$ -picoline to  $\text{Cu}(\text{facam})_2$  was in the range 0–1.0, three isosbestic points were present indicating the formation of a mono-adduct. The spectral change of  $\text{Cu}(\text{facam})_2$  due to the other pyridines except  $\alpha$ -picoline is resemble to that shown in Fig. 1. The plots of  $C_A/(A-A_0)$  vs.  $1/C_B$  are shown in Figs. 2, 3, and 4. The formation constants and

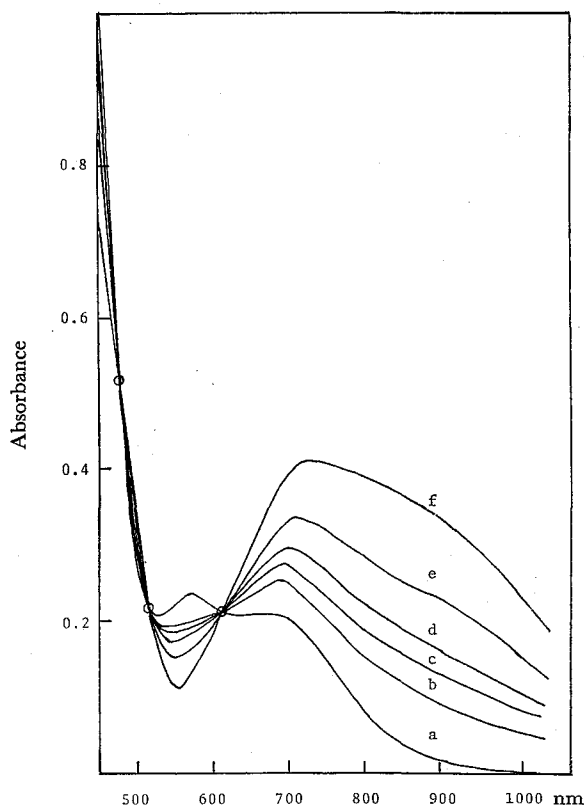


Fig. 1. Spectral change of  $\text{Cu}(\text{facam})_2$  in benzene caused by the addition of  $\beta$ -picoline at  $15^\circ\text{C}$ .  $C_A = 4.90 \times 10^{-3} \text{ M}$ , ratio of  $C_B/C_A$ ; (a) 0; (b) 0.18; (c) 0.28; (d) 0.37; (e) 0.56; (f) 0.92.

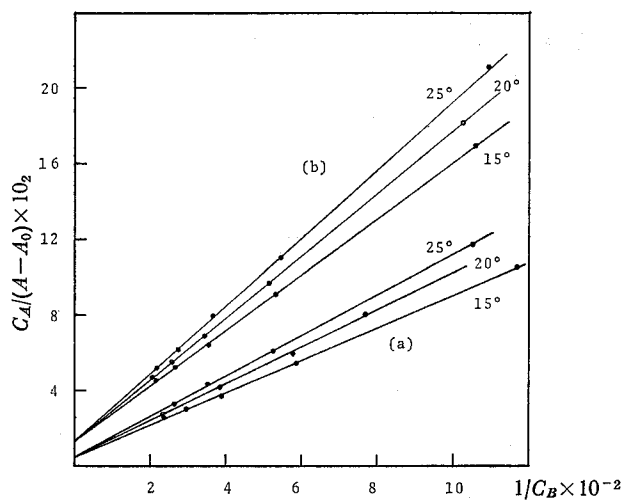


Fig. 2. Plots of  $C_A/(A-A_0)$  vs.  $1/C_B$  for pyridine and  $\alpha$ -picoline at 700 nm. (a) pyridine (b)  $\alpha$ -picoline.

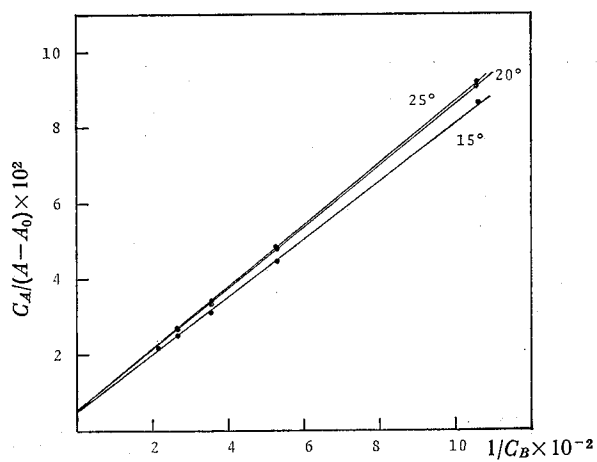


Fig. 3. Plots of  $C_A/(A-A_0)$  vs.  $1/C_B$  for  $\beta$ -picoline at 700 nm.

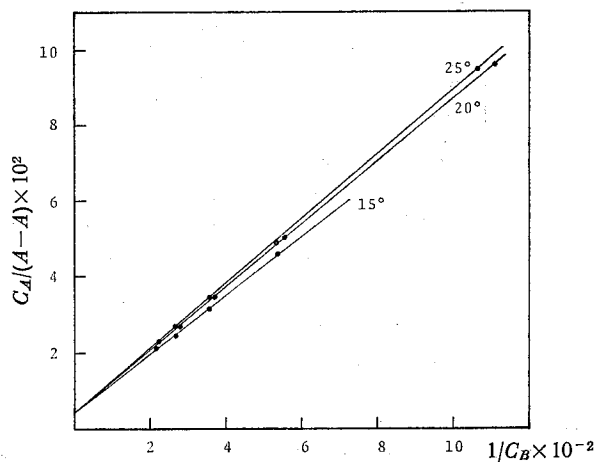


Fig. 4. Plots of  $C_A/(A-A_0)$  vs.  $1/C_B$  for  $\gamma$ -picoline at 700 nm.

Thermodynamics of Adduct-Formation of *Bis*( $\beta$ -diketonato)copper(II)

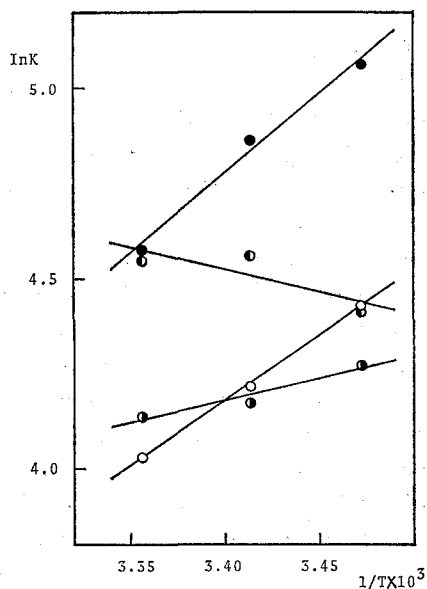


Fig. 5. Plots of  $\ln K$  vs.  $1/T$ .  $\circ$  pyridine;  $\bullet$   $\alpha$ -picoline;  $\bullet$   $\beta$ -picoline;  $\bullet$   $\gamma$ -picoline.

Table I. Formation Constant and Extinction Coefficient of Mono-Adducts between  $\text{Cu}(\text{facam})_2$  and the Pyridines

Pyridines	Temperature ( $^{\circ}\text{C}$ )	$K_1(\text{M}^{-1})$	$\epsilon_2(1 \cdot \text{M}^{-1} \cdot \text{cm}^{-1})$
Pyridine	25	56.4	265
	20	68.1	244
	15	84.1	234
$\alpha$ -picoline	25	97.4	123
	20	127.3	118
	15	158.2	116
$\beta$ -picoline	25	94.7	226
	20	96.1	227
	15	82.9	255
$\gamma$ -picoline	25	62.8	284
	20	65.2	282
	15	71.8	279

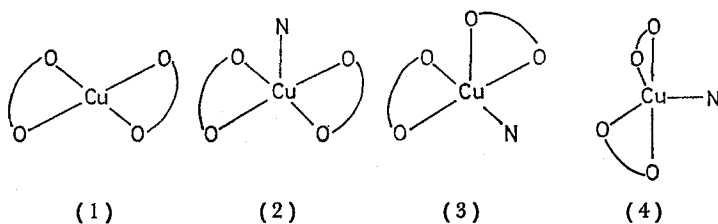
Table II. Thermodynamic Values of Mono-Adducts of the Pyridines with  $\text{Cu}(\text{facam})_2$

Pyridines	$\Delta H$ (Kcal/mol)	$\Delta S$ (e.u.)
pyridine	-6.84	-14.9
$\alpha$ -picoline	-8.30	-18.7
$\beta$ -picoline	2.29	16.8
$\gamma$ -picoline	-2.30	0.5

the extinction coefficients of the mono-adducts estimated from these plots are given in Table I. The plots of  $\ln K$  vs.  $1/T$  are shown in Fig. 5 and the thermodynamic data are given in Table II.

The adducts of pyridine with the fluorinated copper(II) complexes are much more stable than that of  $\text{Cu}(\text{acac})_2$ . This difference is rather due to entropy effect than due to the electron-withdrawing effect of the  $\text{CF}_3$  group.<sup>10)</sup> The enthalpy change for the formation of the mono-adduct of  $\text{Cu}(\text{facam})_2$  with pyridine is similar to that of the  $\text{Cu}(\text{tfa})_2$ -pyridine mono-adduct ( $\Delta H = 7.1$  Kcal/mol).<sup>10)</sup> The entropy change lies in the middle of those for  $\text{Cu}(\text{acac})_2$  ( $\Delta S = -16$  or  $-18$  e.u.) and  $\text{Cu}(\text{tfa})_2$  ( $\Delta S = -11.5$  e.u.).<sup>5,10)</sup> While the thermodynamic data of the  $\text{Cu}(\text{facam})_2$ -pyridine system are convincing, those of the mono-adducts with  $\beta$ - and  $\gamma$ -picolines are unusual. In  $\text{Cu}(\text{acac})_2$ , the enthalpy change of the mono-adducts increases in the order pyridine  $>$   $\beta$ -picoline  $>$   $\gamma$ -picoline.<sup>5)</sup> In  $\text{Cu}(\text{tfa})_2$ , the enthalpy change of pyridine is similar to that of  $\gamma$ -picoline.<sup>10)</sup> The  $\Delta H$  value of  $\text{Cu}(\text{facam})_2$  system increases in the order  $\beta$ -picoline  $>$   $\gamma$ -picoline  $>$  pyridine. The formation reaction of  $\beta$ -picoline is endothermic. These suggest that the rigid and bulky 3-trifluoroacetyl-*d*-camphor hinders the formation of the mono-adducts with  $\beta$ - and  $\gamma$ -picolines. On the other hand, the high stability of the mono-adduct with  $\alpha$ -picoline is due to the small  $\Delta H$  value. This suggests that the mono-adduct has a structure relieving the steric hindrance of the methyl group in  $\alpha$ -position of basic  $\alpha$ -picoline.

The structure of the mono-adducts in solution can be tentatively concluded through the  $\Delta S$  values. The structure of bis( $\beta$ -diketonato)copper(II) in benzene is a square-planar form (1), and the complex is solvated from up and down sides. The mono-adduct of  $\text{Cu}(\text{acac})_2$  with quinoline has a square-pyramidal form (2).<sup>14)</sup> We can suppose another square-pyramidal structure (3), but since (2) and (3) involve displacement of solvent from only one side, the entropy change of both mono-adduct formations would be similar. Another possibility is that two oxygen atoms occupy



apical sites in a trigonal-bipyramidal form (4). (4) would involve displacement of solvent from both sides of the original planar molecule, so providing an explanation for the increased entropy change of the five-coordinate adduct of  $\text{Cu}(\text{tfa})_2$ .<sup>10)</sup> The thermodynamic data of the mono-adduct of  $\text{Cu}(\text{facam})_2$  with pyridine suggest that the complex is a trigonal-bipyramidal form. The structure of the mono-adducts of  $\beta$ - and  $\gamma$ -picolines which give resemble spectral changes to that of the pyridine system also is a trigonal-bipyramidal in essence, while it is concluded that the molecules are very distorted due to the bulky and rigid 3-trifluoroacetyl-*d*-camphor ligand.

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